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LETTERS

A new synthetic protocol for the direct preparation of organomanganese reagents; organomanganese tosylates and mesylates

Seung-Hoi Kim and Reuben D. Rieke *

Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0304, USA

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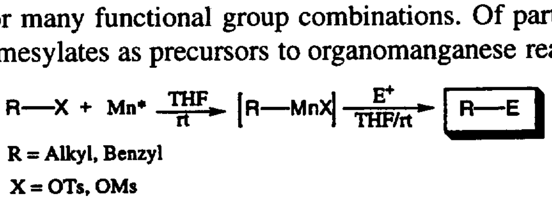
Abstract

A new synthetic route to organomanganese sulfonate reagents has been developed. These useful reagents can be readily prepared via direct oxidative addition of highly reactive manganese to carbon–oxygen bonds of the corresponding tosylates and mesylates under mild conditions. © 1999 Elsevier Science Ltd. All rights reserved.

Until recently, the most widely used approach for the preparation of organomanganese compounds was the metathesis of organolithium or Grignard reagents.[1] This approach allows limited functionality in the organic moiety. Recently, the advent of Rieke manganese[2] and Mn–graphite[3] have allowed the preparation of organomanganese reagents via direct oxidative addition of manganese metal to carbon–halogen bonds. This approach tolerates a much wider spectrum of functional groups in the organic moiety. In fact, the highly reactive manganese (Mn*) prepared via the lithium–naphthalene reduction method represents the most reactive metal towards oxidative addition of all the metals prepared by this method.[4] Considering the high reactivity of the active manganese metal prepared by this approach, we explored the possibility of the oxidative addition to carbon–oxygen bonds. Few reports exist on the oxidative addition of main group or even transition metals to carbon–oxygen bonds.[5] However, the synthetic advantages to such an approach are obvious as the conversion of alcohols into halides can be extremely problematic for many functional group combinations. Of particular interest would be the availability of tosylates and mesylates as precursors to organomanganese reagents (Scheme 1).



Scheme 1.

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* Corresponding author.

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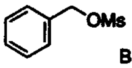
Table 1
Cross-coupling reaction of benzylic and functionalized benzylic manganese sulfonates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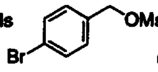
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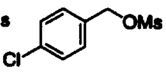
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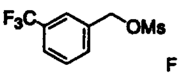
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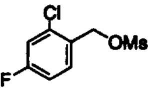
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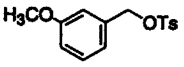
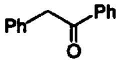
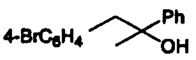
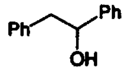
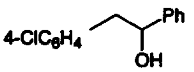
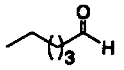
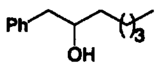
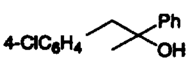
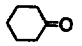
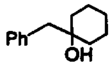
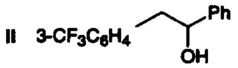
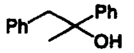
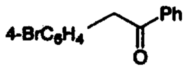
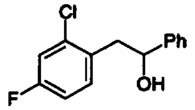
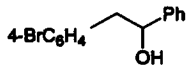
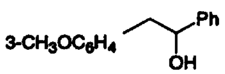

2f

Entry	Sulfonate[a]	E[b]	Product[c]	Yield(%)[d]	Entry	Sulfonate[a]	E[b]	Product[c]	Yield(%)[d]
1	2a	I[e]		63[e]	8	2b	III		80
2	2a	II		72	9	2c	II		95
3	2a			50	10	2c	III		92
4	2a			29	11	2d	II		89
5	2a	PhCOCH$_3$		36					
6	2b	I[e]		50[e]	12	2e	II		92
7	2b	II		90	13	2f	II		94

[a] For the preparation, see: ref 6 [b] Electrophile; I : Benzoyl Chloride, II : Benzaldehyde, III : Acetophenone
[c] All of the products were fully characterized by ^1H, ^{13}C NMR, FTIR and HRMS.
[d] Isolated yields (based on electrophile unless otherwise mentioned)
[e] Excess benzoyl chloride was used (yield was based on mesylate)

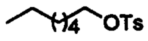
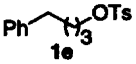
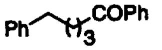
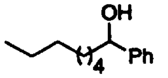
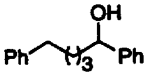
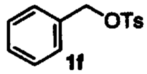
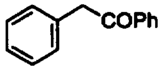
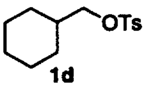
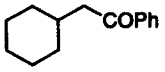
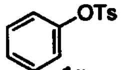
We would like to report that Mn* does, in fact, undergo oxidative addition to alkyl and benzylic tosylates and mesylates under mild conditions to yield the corresponding organomanganese tosylates and mesylates in excellent yields. To our knowledge, this is the first example of organomanganese tosylates and mesylates prepared via direct oxidative addition of manganese metal or by any metathesis approach.

To investigate the new protocol, a variety of benzyl sulfonates[6] were examined with active manganese.[7] The oxidative addition of active manganese to benzyl mesylate was easily completed at room temperature in only 30 min. The resulting benzylic manganese mesylates were cross-coupled with several electrophiles. The coupling reactions were completed under mild conditions and significantly in the absence of any transition metal catalyst. With the preliminary results from non-functionalized benzylic mesylate, functionalized benzylic mesylates containing a halogen atom have been investigated to expand this methodology. The results are summarized in Table 1.

From these results, it can be inferred that the present conditions tolerate halogen atoms attached to the aryl group of the benzyl mesylates. Of special interest is entry 11 in Table 1, clearly this approach tolerates the presence of a trifluoromethyl group.

As shown in Table 2, the oxidative addition to alkyl tosylates[8] was also investigated. The oxidative addition was easily completed by simple treatment of Mn* with the alkyl tosylate at room temperature in THF. Unfortunately, no reaction was found to occur with phenyl tosylate even at refluxing temperatures (entry 9, Table 2). The formation of organomanganese tosylates was also confirmed by the subsequent cross-coupling reaction with different electrophiles. The tosylates listed in Table 2 reacted with benzoyl

Table 2
Preparation of organomanganese tosylates and their coupling reaction

Entry	Tosylate	E[a]	Product[b]	Yield(%)[c]	Entry	Tosylate	E[a]	Product[b]	Yield(%)[c]
1	 **1a**	I		48	6	 **1e**	I		48
2	**1a**	II		64	7	**1e**	II		36
3	 **1b**	I		57					
4	 **1c**	I		44	8	 **1f**	I		74[d]
5	 **1d**	I		86	9	 **1g**		—	0[e]

[a] Electrophile; I : Benzoyl chloride, II : Benzaldehyde
[b] All of the products were fully characterized by ^{1}H, ^{13}C NMR, FTIR and HRMS.
[c] Based on electrophile unless otherwise mentioned [d] Excess benzoyl chloride was used (yield was based on tosylate)
[e] No oxidative addition was occured

chloride to yield the corresponding ketones. The coupling reactions were carried out at room temperature in THF in the absence of any transition metal catalyst. The results are summarized in Table 2. Moderate to excellent yields (44–86%) were obtained. In contrast to all the primary tosylates, a low yield (17%) was obtained from a secondary tosylate. This may be due to the steric hindrance and/or easy elimination of organomanganese tosylate yielding alkenes. This aspect is under further examination. And also, cross-coupling reaction with benzaldehyde gave the corresponding alcohols in moderate yields (36–64%).[9]

In conclusion, a new synthetic route to organomanganese tosylate reagents has been developed. These highly useful reagents can be readily prepared via direct oxidative addition of highly active manganese to the corresponding tosylates under mild conditions. The approach works equally well for primary as well as benzylic tosylates and mesylates. Finally, it should be mentioned that the cross-coupling reaction of the resulting organomanganese reagents is carried out in the absence of any transition metal catalyst.

Acknowledgements

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6. For the preparation of mesylates, see: Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.
7. For the preparation of benzylic metal reagents and their applications, see: Ref. 2f and references cited therein.
8. For the preparation of tosylates, see: Kabalka, G. W.; Varma, M.; Varma, R. S. *J. Org. Chem.* **1986**, *51*, 2386.
9. The following is a representative procedure: to a slurry of Rieke manganese (10.0 mmol) in THF (10 mL) under argon was added benzyl mesylate (9.0 mmol) at room temperature and the mixture was stirred at room temperature for 30 min. 1,2-Dibromoethane (2.0 mmol) was added neat to the reaction mixture at 0°C and the mixture was allowed to warm to room temperature over 5 min. To the resulting organomanganese reagent was added benzaldehyde at room temperature and then the resulting mixture was stirred at room temperature for 30 min. A typical work-up procedure, quenching, washing and column chromatography, was carried out to purify the product.